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(54) Title: PAPER SURFACE SIZING AGENTS, METHOD OF USE AND SURFACE SIZED PAPER (57) Abstract <p>A sizing agent for paper that is a 2-oxetanone multimer which is not a solid at 35 °C, particularly a multimer mixture in which at least 25 weight percent of the hydrocarbon substituents contain irregularities such as branched alkyl groups or linear or branched alkenyl groups. Paper surface sized with the 2-oxetanone multimer sizing agent and the method of surface sizing paper are also disclosed.</p>		

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**PAPER SURFACE SIZING AGENTS,
METHOD OF USE AND SURFACE SIZED PAPER**

Field of the Invention

This invention relates to 2-oxetanone sizing agents, their manufacture and use in sizing paper.

Background of the Invention

The amount of fine paper produced under alkaline conditions has been increasing rapidly, encouraged by cost savings, the ability to use precipitated calcium carbonate (PCC), an increased demand for improved paper permanence, and brightness, and an increased tendency to close the wet-end of the paper machine.

Current applications for fine paper require particular attention to sizing before conversion or end-use, such as adding machine paper and inkjet printer paper, high-speed photocopies, envelopes and forms bond including computer printer paper. The growing popularity of inkjet printers has also focused attention on the sizing requirements for paper intended for this end use application.

The most common sizing agents for fine paper made under alkaline conditions are alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). Both types of sizing agents have a reactive functional group that covalently bonds to cellulose fiber and hydrophobic tails that are oriented away from the fiber. The nature and orientation of these hydrophobic tails cause the fiber to repel water.

Commercial ASA-based sizing agents may be prepared by the reaction of maleic anhydride with an olefin (C_{14} - C_{18}).

Commercial AKDs, containing one β -lactone ring, are prepared by the dimerization of the alkyl ketenes made from two saturated, straight-chain fatty acid chlorides; the

most widely used AKDs are prepared from palmitic and/or stearic acid. Other ketene dimers, such as the alkenyl based ketene dimer (Aquapel® 421 of Hercules Incorporated, Wilmington, Delaware, U.S.A.), have also been used commercially.

Ketene multimers, containing more than one β -lactone ring, have been disclosed as internal sizing agents for paper in Japanese Kokai 168991/89 and 168992/89, both of which are incorporated herein by reference. The ketene multimers are said to show improved sizing compared to the ketene dimers previously used, when applied as an internal size incorporated in the paper pulp slurry. The ketene multimers are prepared from a mixture of mono- and dicarboxylic acids.

EP-A1-0 629 741 discloses alkyl ketene dimer and multimer mixtures as sizing agents in paper used in high speed converting and reprographic machines. The alkyl ketene multimers are made from the reaction of a molar excess of monocarboxylic acid, typically a fatty acid, with a dicarboxylic acid. These multimer compounds are solids at 25°C.

EP-A2-0 666 368 discloses paper for high speed or reprographic operations that is internally sized with an alkyl or alkenyl ketene dimer and/or multimer sizing agent. The preferred 2-oxetanone multimers are prepared with fatty acid to diacid ratios ranging from 1:1 to 3.5:1.

While the sized papers described in EP-A1-0 629 741 and EP-A2-0 666 368 provide superior performance in high speed precision converting and reprographic equipment, there is still a need for alkaline paper that also gives excellent print quality in inkjet printers. The performance criteria for inkjet printer paper, where print quality is paramount, are quite different from those for paper intended for high speed precision

converting or reprographic applications, where machine-feed problems are a major concern.

5 Inkjet print quality for black ink can be evaluated using the following criteria: black line growth, typically measured on a 1-10 scale with low numbers representing narrow lines with sharp edges (a desirable characteristic) and high numbers representing broad fuzzy lines, usually caused by ink wicking in the paper; front optical density, a measure of the density (darkness) of a
10 test area on the printed, front side of paper that is printed solid with black ink; and back optical density, a measure of the amount of ink that penetrates the paper to the unprinted, back side of the paper.

15 The criteria for black ink printing also apply to color ink printing on inkjet printers. In addition, color inkjet printing can be evaluated for color-to-color bleed of adjacently printed colors, typically using a 1-5 scale in which low numbers indicate little or no color-to-color bleed or mixing (desirable) and high numbers indicated bleeding of
20 adjacently printed colors. The objective of minimal color-to-color bleed for color inkjet printing requires paper quality characteristics, i.e., ink absorbency and hold-out, that are different from the balance sought for black ink printing.

25 Improvements in inkjet printing quality may theoretically be made by modifications in the inkjet printer itself or the ink formulation; by modifications in paper furnish or papermaking; and/or by papermaking additives. The papermaking industry is seeking means for improving the
30 paper used for inkjet printing as a result of the increased demand for inkjet printers in the marketplace. The increased popularity of inkjet printers has been coupled with user expectations that print quality should be measured against the high performance standards for laser printers,

the most commonly used high letter quality printers in the marketplace.

There is consequently a need for alkaline fine paper, alkaline sizes and sizing methods that not only provide superior performance in high speed precision converting and reprographic equipment but also provide excellent print quality in inkjet printers, particularly inkjet printers used for black ink printing. The present invention satisfies this need.

Summary of the Invention

One aspect of the invention is a sizing agent which is a 2-oxetanone multimer that is not a solid at a temperature of 35°C and that is prepared from a reaction mixture of fatty acid and dicarboxylic acid having a molar excess of dicarboxylic acid. These 2-oxetanone multimers are particularly useful as sizing agents, most particularly as surface sizing agents for paper (also sometimes called external sizing agents).

Another aspect of the invention is a method of sizing paper by surface sizing paper with a sizing agent that is a 2-oxetanone multimer that is not a solid at a temperature of 35°C.

Yet another aspect of the invention is paper surface sized with these 2-oxetanone multimer sizing agents.

The method of this invention for surface sizing paper made under alkaline conditions provides levels of sizing in surface sized alkaline fine paper that give not only excellent print quality in inkjet printing end use applications but also excellent performance in high speed precision converting and reprographic equipment.

As used herein, "percent" or "%" means, with respect to components or ingredients of a compound, composition or mixture, the weight of the component or

ingredient based on the weight of the compound, composition or mixture containing it, unless otherwise indicated.

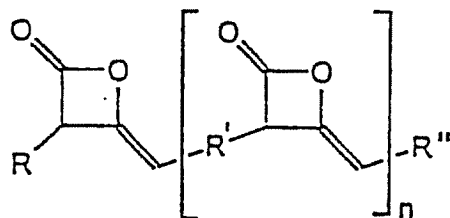
Detailed Description of the Preferred Embodiments

The present invention includes a sizing agent that comprises a 2-oxetanone-based multimer sizing agent (herein also referred to as 2-oxetanone multimer sizing agent or ketene multimer sizing agent) that at 35°C is not a solid (not substantially crystalline, semi-crystalline, or waxy solid; *i.e.*, it flows on heating without heat of fusion); paper treated with a surface sizing treatment comprising such sizing agent; and a method of making the sized paper using such sizing agent.

More preferably, the 2-oxetanone multimer compound according to the invention is a liquid at 35°C, more preferably at 25°C and most preferably at 20°C. (The references to "liquid" of course apply to the sizing agent *per se* and not to an emulsion or other combination containing the sizing agent.)

The invention preferably comprises a 2-oxetanone-based multimer sizing agent having irregularities in the chemical structure of its pendant hydrophobic constituents; *i.e.*, the chemical structure contains irregularities such as carbon-to-carbon double bonds or branching in one or more of the hydrocarbon chains. (Conventional alkyl ketene dimers are regular in that they have saturated straight-chain hydrocarbon chains).

The surface sizing agent of this invention is preferably a 2-oxetanone multimer having the formula (I)



(I)

in which n is an integer of at least 1, preferably 1 to about 20 and more preferably about 1 to about 8. (In the formula (I), when n is 0, such compound is termed a 2-oxetanone dimer or ketene dimer.) The surface sizing agent of this invention may also be a mixture of 2-oxetanone multimers of formula (I). The ketene multimer mixtures of this invention are prepared from a mixture of fatty acid and a dicarboxylic acid in a mole ratio of about 1:1 to about 1:5 fatty acid to dicarboxylic acid.

Mixtures of the 2-oxetanone multimers preferably contain regio isomers of such multimer compounds and preferably contain an average n of from about 1 to about 8, more preferably from greater than about 1 to about 8, and even more preferably from about 2 to about 6, and with an average of about 2 to about 4 being the most presently preferred. Such mixtures of 2-oxetanone multimers may also contain some 2-oxetanone dimer, i.e., $n=0$ in formula (I), as a consequence of the preparation method (described below) used to make the multimers.

R and R'' are substantially hydrophobic in nature, are acyclic, are preferably hydrocarbons of at least about 4 carbon atoms in length and may be the same or different. R and R'' are more preferably about C_{10} - C_{20} and most preferably about C_{14} - C_{16} .

R and R'' , which may be the same or different, are preferably independently selected from the group of straight (linear) or branched alkyl or straight (linear) or branched alkenyl, provided that at least one of R and R'' is not straight chain (linear) alkyl. R and R'' are more preferably linear alkenyl. Preferably at least 25% by weight of the sizing agent comprises the 2-oxetanone structure in which at least one of R and R'' is not straight chain (linear) alkyl. R and R'' are ordinarily derived from a monocarboxylic acid reactant, e.g., fatty acid and preferably an unsaturated fatty acid, when the ketene multimer is prepared from

reaction of a monoacid component with a diacid component, as described below.

R' may be a branched, straight chain, i.e., linear, or alicyclic, i.e., cyclic-containing, saturated or unsaturated hydrocarbon and is preferably a hydrocarbon of from about 1 to about 40 carbon atoms. R' may more preferably be selected from about C₂-C₁₂ and most preferably from C₄-C₈; in such cases, R' is preferably a straight chain alkyl. Alternatively, R' may more preferably be selected from about C₂₀-C₄₀ and most preferably from about C₂₈-C₃₂; R' is preferably branched or alicyclic for the more preferred about C₂₀-C₄₀ and most preferred about C₂₈-C₃₂.

R' is ordinarily derived from a dicarboxylic acid reactant when the ketene multimer is prepared from reaction of a monoacid component with a diacid component, as described below.

The 2-oxetanone multimer is preferably a mixture of 2-oxetanone multimers, particularly a mixture of 2-oxetanone multimers where at least about 25 weight percent, more preferably at least about 50 weight percent and most preferably at least about 75 weight percent, of the mixture is multimers containing hydrocarbon substituents with irregularities that may be branched alkyl, linear alkenyl or branched alkenyl.

The alkaline sizing agents of the present invention, that give improved print quality performance in typical inkjet printing end use applications, have a reactive 2-oxetanone group and pendant hydrophobic hydrocarbon tails. In that respect, they resemble traditional AKD-based sizing agents, but unlike the saturated straight chains in the fatty acids used to prepare conventional solid alkyl ketene dimer or multimer based sizing agents, the hydrocarbon chain in one or both of the fatty acid chlorides used to prepare this class of sizing agents contain irregularities in the chemical structure of

the pendant hydrocarbon chains, such as carbon-to-carbon double bonds and chain branching. Due to the irregularities in the pendant hydrocarbon chains, these sizing agents are not solid, and preferably are liquid, at or near room temperature, i.e., about 25°C.

The 2-oxetanone multimer surface sizing agents of this invention may be formed from mixtures of a fatty acid and a dicarboxylic acid. Preferred exemplary fatty acids include oleic (octadecenoic), linoleic (octadecadienoic), palmitoleic (hexadecenoic), linolenic (octadecatrienoic), isostearic and mixtures of these and/or other fatty acids. Preferred commercially available fatty acids are Pamak®-1, Pamak®-131 or Pamolyn® 380 liquid fatty acids (fatty acid mixtures available from Hercules Incorporated, Wilmington, Delaware, U.S.A.) and comprising primarily oleic acid and linoleic acid. Other exemplary fatty acids that may be used are the following unsaturated fatty acids: dodecenoic, tetradecenoic (myristoleic), octadecadienoic (linolelaidic), eicosenoic (gadoleic), eicosatetraenoic (arachidonic), cis-13-docosenoic (erucic), trans-13-docosenoic (brassidic), and docosapentaenoic (clupanodonic) acids and mixtures of such fatty acids.

More preferably, the 2-oxetanone multimer sizing agent made from the foregoing types of fatty acids, i.e., containing irregularities such as unsaturation or branching, is at least 25% of the sizing agent, more preferably at least about 50% and most preferably at least about 70%.

Dicarboxylic acids that may be used to form the 2-oxetanone multimers of this invention include azelaic acid, sebacic acid and dodecanedioic acid, all of which are preferred; mixtures of dicarboxylic acids may also be used. Dicarboxylic acids made by the dimerization of unsaturated (monocarboxylic) fatty acids may also be used where the resultant dicarboxylic acid is preferably a C₂₄-C₄₄ dicarboxylic acid, and more preferably a C₃₂-C₃₆

dicarboxylic acid. In situations where the dicarboxylic acid is a fatty acid dimer, the branching and/or cyclic-structure of such fatty acid dimers contributes to the irregularities present in the resultant 2-oxetanone multimer sizing agent.

The ketene multimers of this invention may be defined by the molar ratio of fatty acid component to dicarboxylic acid component used to prepare the ketene multimers. The length of a ketene multimer oligomer, *i.e.*, the value of *n* in the formula noted above, is a function of the molar ratio of fatty acid to dicarboxylic acid used to form the multimer.

Such ketene multimers are ordinarily a mixture of ketene multimers, with different chain lengths; some ketene dimer may also be present in the mixture, as mentioned previously, although such ketene dimer is unnecessary in the present invention. The 2-oxetanone multimers of this invention are preferably mixtures containing *n* averaging from about 1 to about 8, more preferably from greater than about 1 to about 8, and even more preferably from about 2 to about 6, and with an average *n* of about 2 to about 4 being the most presently preferred. The average value for *n* for a mixture of 2-oxetanone multimers may be calculated from molecular weights determined by size exclusion chromatography, also called gel permeation chromatography, a technique well known to those skilled in the art. 2-Oxetanone multimers having a specific *n* value, *e.g.*, *n*=3, may be recovered or isolated from the ketene multimer mixtures by conventional separation techniques.

The mole ratio of the fatty acid component to the dicarboxylic acid component in the reaction mixture of such components used to form the multimers is preferably from about 1:1 to about 1:5, more preferably from about 1:1 to about 1:4 and most preferably from about 1:1 to about 1:3. More preferably, the mole ratio of fatty acid component to

dicarboxylic acid component is one which provides an excess of diacid (dicarboxylic acid compound) as compared with the monoacid (fatty acid) component. Preferred examples are 2-oxetanone multimers prepared from mixtures of Pamak®-131 and diacids selected from azelaic acid, sebacic acid, dodecanedioic acid or mixtures thereof having mole ratios of from about 1:1 to about 1:4 monoacid to diacid.

For use as surface sizing agents for the more preferred alkaline fine paper, the mole ratio of the fatty acid component (monoacid) to the dicarboxylic acid component (diacid) is preferably about 1:1 to about 1:5; more preferably, the mole ratio is one that provides a molar excess of the dicarboxylic acid component up to about 1:5 monoacid to diacid. More preferably, the mole ratio is about 1:1.5 to about 1:4, and most preferably about 1:2 monoacid to diacid.

These surface sizing agents may be prepared by known procedures; see, e.g., EP-A2-666,363, Japanese Kokai 168991/89 and Japanese Kokai 168992/89, the disclosures of which are incorporated herein by reference. In the first step, acid chlorides from a mixture of fatty acid and dicarboxylic acid are formed, using phosphorous trichloride or another conventional chlorination agent. In an alternative procedure, the acid chlorides may be prepared separately or sequentially from the fatty acid component and the dicarboxylic acid component. The acid chlorides in the reaction mixture are then dehydrochlorinated in the presence of triethylamine or another suitable base, to form the 2-oxetanone multimer mixture. Stable emulsions of these surface sizing agents can be prepared in the same way as standard AKD emulsions.

The surface sizing agents of this invention are employed as aqueous emulsions thereof which are generally prepared with the aid of emulsifying agents such as cationic or ordinary starches, carboxymethylcellulose, natural gums,

gelatin, cationic polymers or polyvinylalcohol, all of which serve as protective colloids. The preferred emulsifying agent is a cationic starch or a cationic starch derivative. The emulsifying agents may optionally be used with
5 surfactants, and the preferred surfactant is sodium lignosulfonate. Non-limiting examples of other surfactants that are optionally useable with the emulsifying agent include polyoxyethylene-based surfactants such as polyoxyethylene sorbitan trioleate, polyoxyethylene sorbitol
10 hexaoleate, polyoxyethylene sorbitol laurate and polyoxyethylene sorbitol oleate-laurate.

Aqueous emulsions of the surface sizing agent are employed since it is desirable for the sizing agents to be uniformly dispersed throughout the aqueous medium in order
15 to obtain good sizing results. The aqueous emulsion of surface sizing agent is generally in the form of minute particles of surface sizing agent, each surrounded by a stabilizing coating or layer of emulsifying agent, e.g., cationic starch. The aqueous emulsion containing the
20 surface sizing agent may be prepared by the following procedure. The emulsifier is typically first dispersed in water, along with the optional surfactant if used, and the surface sizing agent is then introduced with vigorous agitation. The presence of the emulsifying agent generally
25 makes high speed agitation or mechanical homogenizers unnecessary for creation of a stable aqueous emulsion.

The amount of surface sizing agent employed in the aqueous emulsion may vary over wide ranges, e.g., from about 0.1% to about 50% by weight, with at least about 5% by
30 weight being preferred. The emulsifying agent in the aqueous emulsion is generally employed in a weight ratio to the sizing agent of about 1:40 to about 4:1, preferably from about 1:8 to about 1:1.

The invention also comprises paper made under acid
35 or alkaline papermaking conditions, preferably the latter,

and surface sized with the 2-oxetanone-based multimer sizing agent, that is, with a ketene multimer sizing agent containing the 2-oxetanone functionality.

Preferably the invention further comprises
5 alkaline paper that is surface treated with the 2-oxetanone based sizing agent according to the invention and contains a water soluble inorganic salt of an alkali metal, preferably NaCl, as well as alum and precipitated calcium carbonate (PCC). However, the paper of this invention will often be
10 made without NaCl.

The surface sized paper of this invention may be any fine paper grade that ordinarily requires sizing. Such paper includes continuous forms bond paper, copy paper, envelope-making paper, offset printing paper, inkjet
15 printing paper, as well as precision converted products, such as envelopes and adding machine paper.

The surface sizing agent and method of this invention may also be employed with any other types of paper, including paper made under acid or alkaline
20 papermaking conditions and including without limitation newsprint, paperboard such as liquid packaging paperboard, recycled liner paperboard, for example, and molded paper end-use applications that require sizing, and other paper products. Such applications include gluing with water-based
25 adhesives, inkjet printing and offset printing.

The present invention also relates to a method of sizing paper by surface sizing paper with the 2-oxetanone multimer sizing agents of the invention.

The surface sizing agents of this invention are
30 applied via known surface sizing (also called external sizing) procedures being applied externally to the preformed paper. Surface sizing ordinarily involves addition of the sizing agent at a size press on a paper machine, where the sizing agent is applied to or metered onto the surface of
35 the paper. Alternatively, surface sizing may be carried out

by addition of the sizing agent at the calender stack, or by spraying, or by other coating techniques. The surface sized paper is typically dried at elevated temperatures using known drying techniques.

5 The surface sizing agent of this invention is preferably applied to the surface of paper being surface sized in an amount of at least about 0.0025 wt%, based on the weight of the dry sized paper. Paper surface sized with the 2-oxetanone multimer sizing agent of this invention
10 preferably has from about 0.0025 wt% to about 0.5 wt%, more preferably, from about 0.005 wt% to about 0.2 wt% and most preferably, about 0.01 to about 0.1 wt% sizing agent present on the dry sized paper, based on the weight of the dry surface sized paper.

15 Water or any aqueous solution of size press additive may be used in combination with the sizing agent of this invention, when added at the size press. Addition levels of starch in the size press may range from 0 to about 100 kg/mtonne of dry sized paper. Size press starches
20 suitable for use with the sizing agent of this invention include ethylated starch, oxidized starch, ammonium persulfate converted starch, enzyme converted starch, cationic starch and the like.

 The addition of the 2-oxetanone multimer sizing
25 agent of this invention at the size press or via other means for surface sizing of paper provides satisfactory sizing performance without the need for an internal sizing agent. However, internal sizing agents may be used if desired. In the event that an internal sizing agent is employed, the
30 internal size addition level for paper of this invention is preferably at least about 0.05 kg/mtonne (0.005 wt%), more preferably at least about 0.25 kg/mtonne (0.025 wt%) and most preferably at least about 0.5 kg/mtonne (0.05 wt%), all based on the weight of the dry sized paper. The internal
35 sizing agent may be any conventional paper sizing agent and

preferred internal sizing agents include alkyl ketene dimer, alkyl ketene multimer, alkenyl ketene dimer, alkenyl ketene multimer, alkyl succinic anhydride, alkenyl succinic anhydride, rosin and mixtures of these. In addition, the internal sizing agent may be employed with paper made under neutral pH or acid conditions and may include acid-rosin sized paper.

Although the 2-oxetanone multimers of this invention are preferably employed as surface sizing agents, they may also be used as internal sizing agents for paper.

The invention will now be described with reference to the following specific, non-limiting examples.

Experimental Procedures

The 2-oxetanone sizing agents, including the multimers, were prepared by methods used conventionally to prepare commercial alkyl ketene dimers (AKDs); i.e., acid chlorides from a mixture of fatty acid and dicarboxylic acid were formed, using a conventional chlorination agent, and the acid chlorides were dehydrochlorinated in the presence of a suitable base.

A general procedure for preparation of a 2-oxetanone product on a laboratory scale from a monocarboxylic fatty acid and a dicarboxylic acid, such as azelaic acid or a fatty acid dimer acid, is as follows. The mole ratio of monocarboxylic fatty acid component to dicarboxylic acid component is selected depending on whether a predominance of ketene dimer or a predominance of ketene multimer is desired. For ketene multimers with an average n of from about 1 to 6, a preferred mole ratio of monocarboxylic fatty acid to dicarboxylic acid is from about 1:1 to 1:4.

The fatty acid component is introduced to a stirred reactor, blanketed with nitrogen, and heated to

about 70°C. The dicarboxylic acid component, if a liquid, is added directly to the reactor with the fatty acid, or, if a solid, is added gradually with stirring, to form a mixture of the two components. The two component mixture is then chlorinated at a temperature of about 65-70°C with phosphorous trichloride, by gradual introduction of the PCl_3 chlorination agent over 15-30 minutes or more. After addition of the PCl_3 , the chlorinated reaction product is stirred for an additional 15 minutes and then allowed to settle. Phosphorous acids that form as a byproduct of the chlorination reaction are drained from the bottom of the reactor and then excess PCl_3 reactant is removed from the reaction product by evaporation under vacuum.

Confirmation that acid chlorides are formed in the reaction product made by this procedure may be obtained readily by infrared (IR) determination of the presence of a characteristic acid chloride absorbance at 1800 cm^{-1} . IR determination techniques and apparatus are well known and are commercially available from several sources.

Dehydrochlorination of the acid chlorides to form the desired 2-oxetanone product is carried out in a reactor blanketed with nitrogen. About 1 part (by weight) triethylamine base, typically representing a 5% molar excess of triethylamine, is added to about 2-7 parts (by weight) 1,2-dichloropropane solvent in the reactor with stirring, and both are heated to a temperature of about 30-40°C. About 1-3 parts of acid chloride reaction product in about one-half of that amount of 1,2-dichloropropane is added gradually to the reactor with stirring over about 40 minutes, while maintaining a temperature of about 40-45°C. Approximately two hours after the start of the addition of the acid chloride reaction product, completion of the dehydrochlorination reaction is confirmed with IR, and if the characteristic acid chloride absorbance is detected at

1800 cm^{-1} , additional triethylamine may be added as necessary to complete the dehydrochlorination reaction.

Upon completion of the dehydrochlorination reaction, the reaction mixture is filtered to remove byproduct triethylamine hydrochloride salts formed during the dehydrochlorination reaction. Subsequently, the 1,2-dichloropropane solvent is evaporated under vacuum, and additional triethylamine hydrochloride salts that precipitate are removed by filtration. The recovered product is a mixture which contains predominantly 2-oxetanone multimer or dimer, depending on the specific molar ratios of fatty acid and dicarboxylic acid employed as the initial reactants. For use as a sizing agent, an emulsion of the 2-oxetanone product is prepared.

The 2-oxetanone sizing agent emulsions, including the multimer emulsions, were prepared according to the disclosure of U.S. Patent 4,317,756, which is incorporated herein by reference, with particular reference to Example 5 of the patent.

A sizing agent emulsion of a ketene multimer (or dimer) may be prepared by admixing 880 parts of water, 60 parts of cationic corn starch and 10 parts of sodium lignin sulfonate. The mixture is adjusted to pH of about 3.5 with sulfuric acid. The resulting mixture is heated at 90°-95°C for about one hour. Water is then added to the mixture in an amount sufficient to provide a mixture of 1750 parts (total weight). About 240 parts of the ketene multimer (or dimer) is stirred into the mixture together with 2.4 parts of thiadiazine preservative. The resulting premix (at 65°C) is homogenized in one pass through an homogenizer at 3000 p.s.i. The homogenized product is diluted with water to a ketene multimer (or dimer) solids content within the range of about 6% to about 30% to form a sizing agent emulsion; it should be understood that the precise solids content of the sizing agent emulsion is not critical.

The papermaking procedures used to make paper for evaluation of surface sizing, toner adhesion and inkjet quality were as follows. Paper was prepared on a pilot paper machine at Western Michigan University. The paper had a basis weight of 20 lbs./1300 ft² (9.1 kg/121 m²).

To make a typical forms bond paper-making stock, the pulp furnish (three parts hardwood kraft pulp and one part softwood kraft pulp) was refined to 425 ml Canadian Standard Freeness (C.S.F.) using a double disk refiner. Prior to the addition of the filler to the pulp furnish (12% medium particle-size precipitated calcium carbonate), the pH (7.8-8.0), alkalinity (150-200 p.p.m.), and hardness (100 p.p.m.) of the paper making stock were adjusted using the appropriate amounts of H₂SO₄, NaHCO₃, NaOH, and CaCl₂.

Wet-end conditions were as follows: tray pH 7.6-8.0; temperature 49°C; and 180 ppm total alkalinity.

Wet-end additions were made as follows: precipitated calcium carbonate filler (12%) at the first mixing box, quaternary-amine-substituted cationic starch (0.50%) at the first mixing box outlet, alum (0.25%) at the second mixing box outlet valve, and an internal sizing agent at the second mixing box valve.

The internal sizing agent added at the wet-end was a commercially-available alkenyl ketene dimer paper sizing agent, made from a fatty acid feedstock consisting primarily of oleic and linoleic acids, and this was utilized at three different usage levels, 0.1%, 0.125% and 0.15%, all percentages being by weight based on the dry weight of the paper furnish. Stock temperature at the white water tray and head box was controlled at 49°C (120°F).

The wet presses were set at 40 p.s.i. gauge (207 cm Hg). A dryer profile that gave 1-2% moisture at the size press and 4-6% moisture at the reel was used (77 ft/min (23 m/min)). Before the size press, the sizing level was measured on a sample of paper torn from the edge of the

sheet, using the Hercules Size Test (HST). The Hercules Size Test (HST) is a standard test in the industry for measuring the degree of sizing. This method employs an aqueous dye solution as the penetrant to permit optical detection of the liquid front as it moves through the sheet. The apparatus determines the time required for the reflectance of the sheet surface not in contact with the penetrant to drop to a predetermined percentage of its original reflectance. All HST testing data reported measure the seconds to 80% reflection with 1% formic acid ink mixed with naphthol green B dye (Hercules Test Ink #2) unless otherwise noted. The use of this formic acid ink is a more severe test than neutral ink and tends to give faster test times. High HST values are better than low values. The amount of sizing desired depends upon the kind of paper being made and the system used to make it. "Natural aged HST" values were obtained seven days after the paper was sized.

Approximately 50 kg/metric tonne of an oxidized corn starch and 2.5 kg/metric tonne of NaCl were added at the size press (66°C/150°F, pH 8). The surface sizing agent was also added at the size press, in amounts as indicated in the Examples which follow. Calender pressure and reel moisture were adjusted to obtain a Sheffield smoothness of 150 flow units at the reel (Column #2, felt side up).

Example 1

This Example describes the preparation of a mixture of 2-oxetanone multimer compounds from a mixture of fatty acids and a dicarboxylic acid at a mole ratio of 1:2 fatty acid to dicarboxylic acid. In Example 1A, the dicarboxylic acid was a C₃₆ dicarboxylic acid, and in Example 1B, the dicarboxylic acid was azelaic acid.

The chlorination of the fatty acid and dicarboxylic acid mixture was carried out in a 500 mL glass-

jacketed reactor fitted with a condenser, an addition funnel, and nitrogen adapters, which was sparged with nitrogen gas (each piece of glassware having been oven dried at 105°C prior to assembly). The nitrogen gas flow was vented through a NaOH scrubber. The reactor was initially heated to 105°C with a heat gun and cooled under a steady stream of nitrogen.

The dehydrochlorination of the acid chloride reaction product was carried out in a 1 L glass-jacketed reactor fitted with a condenser, an addition funnel, and nitrogen adapters, where was sparged with nitrogen gas (each piece of glassware having been oven dried at 105°C prior to assembly). The reactor was initially heated to 105°C with a heat gun and cooled under a steady stream of nitrogen.

Example 1A: The chlorination of the fatty acid and C₃₆ dicarboxylic acid was carried out as follows. After the 500 mL reactor was cooled to room temperature, 87.8 g (0.31 mole) Pamak®-131 fatty acid mixture (Hercules Incorporated, Wilmington, Delaware, U.S.A.) and 353.1 g (0.62 mole) Unidyme®-14 C₃₆ dicarboxylic acid (Union Camp Corp., Wayne, New Jersey, U.S.A.) were added to the reactor. At this point, the reactor was placed under a static nitrogen blanket instead of a nitrogen gas sweep, i.e., the nitrogen gas flow was stopped. The reactor containing the two liquid components was then heated using a recirculating mineral oil bath set at 70°C. After the temperature of the reactants had reached 65°C, 67.8 mL PCl₃ (1.574 g/mL, B.P. 76°C, Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.) was loaded into the addition funnel and added to the mixture over a period of 30 minutes. Vigorous evolution of HCl was noted, particularly at the beginning of the PCl₃ addition, but little or no exotherm was measured. Fifteen minutes after the addition of PCl₃ was complete, the stirrer was stopped. After ten minutes of settling, 29.9 g of phosphorous acids, a byproduct of the chlorination reaction,

were drained from the bottom of the reactor. Small amounts of phosphorous acids were removed each hour over the next four hours, with a total of 35.4 g phosphorous acids being removed. Finally, excess unreacted PCl_3 was removed on a rotary evaporator (vacuum pump pressure, 60°C) over a 2-hour period. 453.7 g of acid chloride reaction product were isolated, a yield of 97.9%. An I.R. spectrum for the isolated reaction product showed a characteristic acid chloride absorbance at 1800 cm^{-1} .

The dehydrochlorination reaction was carried out as follows. After the 1 L reactor was cooled to room temperature, 440 mL 1,2-dichloropropane solvent (1.156 g/mL, B.P. $95-96^\circ\text{C}$, Fluka Chemical Corp., Ronkonkoma, New York, U.S.A.) and 115.2 mL (0.83 mole) triethylamine (0.726 g/mL, B.P. 88.8°C , Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.) were added to the reactor, the stirrer was started (150 r.p.m.) and the reactor contents were heated to 30°C using a recirculating water bath. At this point, the nitrogen gas flow in the reactor was switched to a nitrogen blanket. A 235.4 g aliquot of acid chloride reaction product was then added to the addition funnel along with 110 mL 1,2-dichloropropane. The contents of the addition funnel were gradually added to the reactor over a period of 40 minutes. Stirrer speed, the temperature of the recirculating water bath, and the addition rate of the acid chloride reaction product were adjusted to control the exotherm and maintain the temperature of the reaction mixture between $40^\circ-45^\circ\text{C}$. The stirrer speed was gradually increased from 150 r.p.m. to 400 r.p.m. over the course of the addition. Two hours after the start of the addition, the reaction was checked for acid chloride by I.R. Completion of the dehydrochlorination reaction is indicated when no acid chloride absorbance at 1800 cm^{-1} is observed. Additional triethylamine may be added to complete the reaction, as necessary.

Once the dehydrochlorination reaction was complete, the reaction mixture was cooled to room temperature (about 25°C) and filtered using a Buchner funnel to remove byproduct triethylamine hydrochloride salts formed by the reaction. Approximately half of the 1,2-dichloropropane solvent in the filtrate was then removed using a rotary evaporator (vacuum pump, 60°C). The reaction product was filtered a second time to remove additional triethylamine hydrochloride salts that had precipitated during evaporation of the 1,2-dichloropropane. The remainder of the 1,2-dichloropropane was then removed on the rotary evaporator (vacuum pump, 60°C, three hours). The reaction product was then filtered a third time to remove any remaining triethylamine hydrochloride salts. Total product yield was 137 g 2-oxetanone multimer product, a yield of 65%. The product was a liquid at 25°C, and analysis by size exclusion chromatography indicated that the mixture of ketene multimers had an average n of about 4.

Example 1B: The chlorination of the fatty acid and azelaic dicarboxylic acid was carried out as follows. After the 500 mL reactor was cooled to room temperature, 140.0 g (0.50 mole) Pamak®-131 fatty acid mixture (Hercules Incorporated, Wilmington, Delaware, U.S.A.) was added to the reactor and heated to a temperature of 70°C. At this point, the nitrogen gas flow in the reactor was switched to a nitrogen blanket. Next, 181 g (1.0 mole) 85% azelaic acid mixture, containing 15% other dicarboxylic acids of different chain lengths (E-1110 from Henkel Corporation's Emery Group, Gulph Mills, Pennsylvania, U.S.A.), were gradually introduced into the reactor with vigorous stirring (250 r.p.m.) over a three minute period. The solid dicarboxylic acid component formed a coarse dispersion with the liquid fatty acid component in the reactor, and the temperature dropped about 10°C during the addition. After the temperature of the reactants reached 70°C, 108 mL PCl₃

(1.574 g/mL, B.P. 76°C, Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.) was loaded into the addition funnel and added to the mixture over a period of 30 minutes. Vigorous evolution of HCl was noted, particularly at the beginning of the PCl₃ addition, but little or no exotherm was measured. The dispersed dicarboxylic acid component dissolved during addition of the PCl₃. Fifteen minutes after the addition of PCl₃ was complete, the stirrer was stopped. After ten minutes of settling, 70.8 g phosphorous acids, a byproduct of the chlorination reaction, were drained from the bottom of the reactor. Small amounts of phosphorous acids were removed each hour over the next three hours, with a total of 71.9 g phosphorous acids (104% of theoretical) being removed. Finally, excess unreacted PCl₃ was removed on a rotary evaporator (vacuum pump pressure, 60°C) over a 2-hour period. 349.6 g of acid chloride reaction product was isolated, a yield of 93%. An I.R. spectrum for the isolated reaction product showed a characteristic acid chloride absorbance at 1800 cm⁻¹, with a small side band being observed at 1710 cm⁻¹.

The dehydrochlorination reaction was carried out as follows. After the 1 L reactor was cooled to room temperature, 500 mL 1,2-dichloropropane solvent (1.156 g/mL, B.P. 95-96°C, Fluka Chemical Corp., Ronkonkoma, New York, U.S.A.) and 286 mL (2.05 mole) triethylamine (0.726 g/mL, B.P. 88.8°C, Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.) were added to the reactor, the stirrer was started (150 r.p.m.) and the reactor contents were heated to 40°C using a recirculating water bath. At this point, the nitrogen gas flow was switched to a nitrogen blanket. A 280.8 g aliquot of acid chloride reaction product was then added to the addition funnel along with 133 mL 1,2-dichloropropane. The contents of the addition funnel were gradually added to the reactor over a period of 40 minutes. Stirrer speed, the temperature of the

recirculating water bath, and the addition rate of the acid chloride reaction product were adjusted to control the exotherm and maintain the temperature of the reaction mixture between 40°-45°C. The stirrer speed was gradually increased from 150 r.p.m. to 400 r.p.m. over the course of the addition. Two hours after the start of the addition, the reaction was checked for acid chloride by I.R. Completion of the dehydrochlorination reaction is indicated when no acid chloride absorbance at 1800 cm^{-1} is observed, although acid anhydride absorbance at 1815 cm^{-1} can complicate this measurement. Additional triethylamine may be added to complete the reaction, as necessary.

Once the dehydrochlorination reaction was complete, the reaction mixture was cooled to room temperature (about 25°C) and filtered using a Buchner funnel to remove byproduct triethylamine hydrochloride salts formed by the reaction. The separated triethylamine salts were reslurried in 150 mL 1,2-dichloropropane at about 25°C to extract any dehydrochlorinated reaction product trapped in the salts and filtered a second time. The filtrates were combined, and approximately half of the 1,2-dichloropropane solvent in the filtrate was then removed using a rotary evaporator (vacuum pump, 60°C). The reaction product was filtered again to remove additional triethylamine hydrochloride salts that had precipitated during evaporation of the 1,2-dichloropropane. The remainder of the 1,2-dichloropropane was then removed on the rotary evaporator (vacuum pump, 60°C, three hours). The total reaction product yield was 175 g 2-oxetanone multimer product, a yield of 82%. The product was a liquid at 25°C, and analysis by size exclusion chromatography indicated that the mixture of ketene multimers had an average n of about 4.

Example 2

This Example describes the use of three ketene multimers of this invention as surface sizing agents.

Four ketene multimers were prepared from Pamak®-
131 fatty acid and azelaic acid mixtures having the
following molar ratios of fatty acid component to
dicarboxylic acid component: 2.5:1, 1:1, 1:2 and 1:4. The
latter two ketene multimers were prepared using a molar
excess of diacid (dicarboxylic acid component) as compared
with the monoacid (fatty acid component). The procedure
used to make the ketene multimer mixtures was similar to
that described in Example 1. The ketene multimer mixtures
were utilized for sizing as aqueous emulsions, prepared as
described under Experimental Procedures.

For comparison, two surface sizing agents were
included as controls, at three usage levels, as shown in
Table 1 below: alkenyl ketene dimer, made from a linoleic
and oleic acid mixture (generally as described above under
Experimental Procedures), and styrene-maleic anhydride
copolymer.

The addition levels of the four ketene multimers
in the size press were 0.005, 0.015 and 0.025 wt%, based on
the weight of the dry sized paper.

In addition to the surface sizing agents utilized
in the size press, an internal sizing agent was also used:
alkenyl ketene dimer (as described above) was added at the
wet end of the papermaking machine, at usage levels of 0.1-
0.15 wt%, based on the weight of dry sized paper.

The results of these surface sizing evaluations
are summarized in Table 1. Sizing efficiencies for the
treated paper that are shown in the Table are measured as
Hercules Sizing Test results, taken at three points: prior
to the size press, at the reel after the size press and
after natural aging for about seven days.

All four of the ketene multimers tested gave large increases in sizing at the reel, after the size press surface sizing treatment, over all usage levels evaluated.

5 Three of the ketene multimers (2.5:1, 1:1, 1:2 fatty acid : diacid ratios) provided sizing differences, at a 0.005 wt% addition level, that were comparable to the alkenyl ketene dimer surface sizing agent control (at 0.005 wt%) and the styrene/maleic anhydride copolymer surface
10 sizing agent control (at 0.05 wt%). The same three ketene multimers, at a 0.025 wt% usage level, provided sizing efficiencies that were comparable to the alkenyl ketene dimer sizing agent control (at 0.025 wt%) and styrene/maleic anhydride copolymer sizing agent (at 0.15 wt%). The ketene
15 multimer with the 1:4 fatty acid to diacid ratio provided smaller, but still significant, increases in sizing efficiency at the reel.

The results for the first three ketene multimers (2.5:1, 1:1, 1:2 fatty acid (FA) to diacid (DA) ratios) indicated that at a given usage level, these ketene multimer
20 surface sizing agents are 6-10 times more effective than a conventional surface sizing agent, the styrene/maleic anhydride copolymer, used as a control.

TABLE 1

SIZING AGENTS		SIZING PROPERTY			INKJET		TONER
Size Press Sizing Agent and Addition Level (wt%)	AKD Internal Size Addition Level (wt%)	HST: before size press (sec)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	
none	0.1	22	3	2	9	1.09	0.40
styrene/maleic anhydride copolymer 0.05	0.1	19	15	10	9	1.13	0.32
alkenyl ketene dimer 0.005	0.1	--	23	19	8	1.11	0.41
alkenyl ketene multimer 2.5:1 FA:DA 0.005	0.1	--	18	14	8	1.11	--
alkenyl ketene multimer 1:1 FA:DA 0.005	0.1	--	22	19	2	1.11	--
alkenyl ketene multimer 1:2 FA:DA 0.005	0.1	13	18	17	8	1.12	0.42
alkenyl ketene multimer 1:4 FA:DA 0.005	0.1	--	10	8	8	1.10	--
styrene/maleic anhydride copolymer 0.15	0.1	--	66	59	8	1.13	0.35

SIZING AGENTS		SIZING PROPERTY			INKJET QUALITY		TONER
Size Press Sizing Agent and Addition Level (wt%)	AKD Internal Size Addition Level (wt%)	HST: before size press (sec)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	Toner Adhesion
alkenyl ketene dimer 0.025	0.1	--	54	39	7	1.15	0.48
alkenyl ketene multimer 2.5:1 FA:DA 0.025	0.1	29	64	39	4	1.13	--
alkenyl ketene multimer 1:1 FA:DA 0.025	0.1	--	68	39	7	1.14	--
alkenyl ketene multimer 1:2 FA:DA 0.025	0.1	14	58	40	7	1.13	0.41
alkenyl ketene multimer 1:4 FA:DA 0.025	0.1	--	40	20	6	1.10	--
none	0.1	20	7	4	8	1.10	0.43
none	0.15	131	59	56	6	1.23	0.48
styrene/maleic anhydride copolymer 0.05	0.15	--	82	90	5	1.25	0.44
alkenyl ketene dimer 0.005	0.15	--	92	91	6	1.27	0.42

SIZING AGENTS		SIZING PROPERTY			INKJET QUALITY		TONER
Size Press Sizing Agent and Addition Level (wt%)	AKD Internal Size Addition Level (wt%)	HST: before size press (sec)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	Toner Adhesion
alkenyl ketene multimer 2.5:1 FA:DA 0.005	0.15	104	85	81	5	1.23	--
alkenyl ketene multimer 1:1 FA:DA 0.005	0.15	--	94	71	7	1.23	--
alkenyl ketene multimer 1:2 FA:DA 0.005	0.15	110	92	64	7	1.21	0.41
alkenyl ketene multimer 1:4 FA:DA 0.005	0.15	--	66	70	5	1.20	--
none	0.15	151	88	84	8	1.28	0.45
styrene/maleic anhydride copolymer 0.15	0.15	147	145	135	2	1.28	0.41
alkenyl ketene dimer 0.025	0.15	133	141	133	5	1.32	0.42
alkenyl ketene multimer 2.5:1 FA:DA 0.025	0.15	--	153	132	5	1.30	--

SIZING AGENTS		SIZING PROPERTY			INKJET QUALITY		TONER
Size Press Sizing Agent and Addition Level (wt%)	AKD Internal Size Addition Level (wt%)	HST: before size press (sec)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	
alkenyl ketene multimer 1:1 FA:DA 0.025	0.15	123	172	140	5	1.31	--
alkenyl ketene multimer 1:2 FA:DA 0.025	0.15	--	133	101	5	1.26	0.45
alkenyl ketene multimer 1:4 FA:DA 0.025	0.15	132	111	99	6	1.25	--
none	0.15	120	43	55	5	1.20	0.44
none	0.125	103	31	15	8	1.15	--
styrene/maleic anhydride copolymer 0.1	0.125	--	77	75	4	1.16	--
alkenyl ketene dimer 0.015	0.125	--	72	63	7	1.17	--
alkenyl ketene multimer 2.5:1 FA:DA 0.015	0.125	51	83	58	7	1.16	--
alkenyl ketene multimer 1:1 FA:DA 0.015	0.125	--	83	73	8	1.21	--

SIZING AGENTS		SIZING PROPERTY			INKJET QUALITY		TONER
Size Press Sizing Agent and Addition Level (wt%)	AKD Internal Size Addition Level (wt%)	HST: before size press (sec)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	Toner Adhesion
alkenyl ketene multimer 1:2 FA:DA 0.015	0.125	102	84	65	6	1.17	--
alkenyl ketene multimer 1:4 FA:DA 0.015	0.125	--	58	56	6	1.16	--
none	0.125	87	14	16	7	1.13	--

Example 3

The surface sized paper produced with the four ketene multimers in Example 2 was evaluated for inkjet printing quality in this Example, using a Hewlett Packard Model 560C Deskjet® inkjet printer. Two inkjet print quality characteristics were measured: black ink line growth and optical density of the printed black ink. Results are summarized in Table 1 in the two columns under "INKJET QUALITY".

Black ink line growth was measured by visual evaluation of line growth by feathering or wicking, i.e., spreading of ink beyond the printed line borders. Print samples were compared to ten samples, ranked as 1-10 with 1 being the best and 10 being the worst quality. Results are summarized in Table 1 above, under the column heading "Black Ink Line Growth".

At the lowest usage level of ketene multimer surface size, all four ketene multimers provided black ink line growth that was at least comparable to a paper with a conventional surface-sizing surface sized at a substantially higher usage level with a styrene/maleic anhydride copolymer surface sizing agent.

At the highest usage level, the ketene multimer surface size provided approximately equivalent black ink line growth as compared to the conventional surface size, but the latter was used at a significantly higher usage level than the ketene multimer size.

Black ink front optical density values were obtained by optical density measurements of black ink printed onto the sized paper, such measurements being made on the front, i.e., printed side of the paper. High optical density values are desirable since they indicate good quality, dense black ink printing. The results, shown in the penultimate column of Table 1, show that the ketene multimer surface sizes generally provide satisfactory black

ink optical density values comparable to the styrene/maleic anhydride copolymer surface sizing agent used at significantly higher usage levels, particularly at the higher internal size levels used concurrently with the ketene multimer surface size.

The results shown in Table 1 indicate that the four ketene multimer surface sizing agents evaluated are cost effective replacements for a conventional polymeric surface sizing agent like styrene/maleic anhydride copolymer, for paper grades requiring good inkjet printing quality.

Example 4

This Example evaluated photocopier toner adhesion on copy paper surface sized with a ketene multimer sizing agent, added at the sizing press.

The ketene multimer was prepared from a reaction mixture containing Pamak®-131 fatty acids and azelaic acid in a 1:2 mole ratio. The procedure used to prepare the ketene multimer was similar to that described in Example 1.

For comparison, two conventional surface sizes were also included in the evaluation. The first was paper sized with a styrene/maleic anhydride copolymer sizing agent, added at the size press at two usage levels, 0.05 and 0.15 wt%, based on the weight of the dry sized paper. Such conventional polymeric sizing agents provide good toner adhesion and were included in this Example as a performance benchmark.

The second surface size included for comparative purposes was paper surface sized with an alkenyl ketene dimer sizing agent, made from a mixture of linoleic and oleic acids, the sizing agent being added at the size press at two usage levels, 0.005 wt% and 0.025 wt%, based on the weight of the dry sized paper. Paper containing no surface size was also included in the evaluation.

An internal size, the alkenyl ketene dimer used as a surface size, was also included as a wet end additive in the papermaking process, at two usage levels, 0.1 wt% and 0.15 wt%, based on the weight of the dry sized paper.

5 Toner adhesion on the sized paper was evaluated using an optical density method that measured the difference in optical density between black toner photocopied onto the front of the (uncreased) paper and the same black photocopied toner with a crack formed by creasing the paper (by folding and unfolding). Poor toner adhesion typically results in formation of a larger width crack at the crease; the difference in the two optical density measurements is therefore large. Low values for the optical density difference indicate good toner adhesion.

10 Results are summarized in Table 1 above, where photocopier toner adhesion values are reported in the last column.

As expected, the polymeric (styrene/maleic acid copolymer) surface-sized paper provided good toner adhesion and the alkenyl ketene dimer surface-sized paper exhibited poorer toner adhesion. Increasing the level of internal size used in combination with the surface size tended to result in reduced toner adhesion.

20 Use of the ketene multimer as a surface sizing agent resulted in mixed but generally satisfactory toner adhesion, with very little difference in toner adhesion from that obtained with the untreated control.

25 Based on these results, ketene multimers are expected to be more efficient sizing agents than traditional polymeric surface sizing agents, without the toner adhesion problems associated with traditional ketene dimer sizing agents.

Example 5

This Example describes the use of two 2-oxetanone multimers of this invention as surface sizing agents. Both alkenyl ketene multimers were prepared from unsaturated fatty acid (monocarboxylic acid) and dicarboxylic acid mixtures having a molar ratio of fatty acid component to dicarboxylic acid component of 1:2. The first ketene multimer was prepared from a mixture of Pamak® 131 fatty acid and azelaic acid, at a 1:2 mole ratio, and the second ketene multimer was prepared from a mixture of Pamak® 131 fatty acid and a C₃₆ fatty acid dimer (dicarboxylic acid), also at a 1:2 mole ratio. The procedure used to make the ketene multimer mixtures was similar to that described in Example 1. The ketene multimer mixtures were utilized for sizing as aqueous emulsions, prepared as described under Experimental Procedures.

Four different addition levels of the two ketene multimer sizing agents were evaluated in the size press: 0.0125, 0.025, 0.05 and 0.10 wt%, based on the weight of the dry sized paper.

For comparison, two surface sizing agents were included as controls, as shown in Table 2 below: alkenyl ketene dimer, made from a linoleic and oleic acid mixture (generally as described above under Experimental Procedures), and styrene-maleic anhydride copolymer.

An additional control having no surface sizing agent at all (only internal sizing as described below) was also included, at three replications.

The surface sizing agents were evaluated at four different addition levels: alkyl ketene dimer sizing agent at 0.0125, 0.025, 0.05 and 0.10 wt%, based on the weight of dry sized paper (these were the same addition levels as used with the two ketene multimer sizing agents), and styrene/maleic acid copolymer at 0.05, 0.10, 0.15 and 0.20 wt%, based on the weight of dry sized paper. These latter

sizing agent levels were higher than that used for the other sizing agents but are nevertheless representative of commercial surface sizing addition rates for this well-known surface sizing agent.

5 In addition to the surface sizing agents utilized in the size press, an internal sizing agent was also used in all of the paper used in this Example: alkenyl ketene dimer (as described above) was added as an internal size at the wet end of the papermaking machine, at usage levels of 0.1-
10 0.15 wt%, based on the weight of dry sized paper.

 The results of these surface sizing evaluations are summarized in Table 2. Sizing efficiencies for the treated paper that are shown in the Table are measured as Hercules Sizing Test results, taken at three points: prior
15 to the size press, at the reel after the size press and after natural aging for about seven days.

 The two alkenyl ketene multimer surface sizes tested gave large increases in sizing over all usage levels evaluated both at the reel and after aging for seven days,
20 as compared with (internally sized) paper that had not been surface sized. The levels of HST sizing were comparable to those obtained with the alkenyl ketene dimer surface size and the styrene/maleic anhydride (SMA) copolymer surface size.

25 Since the SMA copolymer size was used at much higher addition rates than the ketene multimer and ketene dimer surface sizes, these results indicate that alkenyl ketene multimer surface sizes are much more efficient surface sizing agents than a conventional SMA copolymer
30 surface size. As the Examples which follow demonstrate, the alkenyl ketene multimers of the present invention provide comparable black inkjet printing quality compared to SMA copolymer sizing agent and the alkenyl ketene dimer sizing agent, and much better toner adhesion results compared to
35 those obtained with the alkenyl dimer surface size.

TABLE 2

SIZING AGENT		SIZING PROPERTY		INKJET QUALITY		TONER
Size Press Sizing Agent	Surface Size Addition Level (wt%)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	Toner Adhesion
-	-	4	4	FAIR	1.17	0.297
-	-	5	3	POOR/FAIR	1.16	0.289
-	-	5	2	POOR/FAIR	1.16	0.289
styrene/maleic anhydride copolymer	0.05	17	25	FAIR/GOOD	1.30	0.289
styrene/maleic anhydride copolymer	0.10	50	63	FAIR/GOOD	1.31	0.293
styrene/maleic anhydride copolymer	0.15	57	54	GOOD	1.33	-
styrene/maleic anhydride copolymer	0.20	66	66	GOOD	1.32	-
alkenyl ketene dimer	0.0125	53	49	FAIR/GOOD	1.36	0.303
alkenyl ketene dimer	0.025	62	57	FAIR/GOOD	1.33	0.376
alkenyl ketene dimer	0.05	62	48	GOOD	1.39	0.376
alkenyl ketene dimer	0.10	46	85	GOOD	1.42	0.398

SIZING AGENT		SIZING PROPERTY		INKJET QUALITY		TONER
Size Press Sizing Agent	Surface Size Addition Level (wt%)	HST: at reel (sec)	HST: after 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	Toner Adhesion
alkenyl ketene multimer 1:2 FA:azelaic acid	0.0125	49	58	FAIR/GOOD	1.35	0.292
alkenyl ketene multimer 1:2 FA:azelaic acid	0.025	71	74	FAIR/GOOD	1.32	0.293
alkenyl ketene multimer 1:2 FA:azelaic acid	0.05	67	54	GOOD	1.34	0.299
alkenyl ketene multimer 1:2 FA:azelaic acid	0.10	61	136	GOOD	1.42	0.300

SIZING AGENT		SIZING PROPERTY		INKJET QUALITY		TONER
Size Press Sizing Agent	Surface Size Addition Level (wt%)	HST: at reel (sec)	HST: after aging 7 days (sec)	Black Ink Line Growth	Black Ink Front Optical Density	Toner Adhesion
alkenyl ketene multimer 1:2 FA:C36 fatty acid dimer	0.0125	20	27	FAIR	1.27	0.293
alkenyl ketene multimer 1:2 FA:C36 fatty acid dimer	0.025	33	42	FAIR/GOOD	1.30	-
alkenyl ketene multimer 1:2 FA:C36 fatty acid dimer	0.05	46	50	GOOD	1.36	0.309
alkenyl ketene multimer 1:2 FA:C36 fatty acid dimer	0.10	54	60	GOOD	1.29	0.333

Example 6

The surface sized paper produced with the two ketene multimers in Example 5 was evaluated for black inkjet printing quality in this Example, using a Hewlett Packard Model 560C Deskjet® inkjet printer. Two inkjet print quality characteristics were measured: black ink line growth and optical density of the printed black ink. The same evaluation was carried out with the paper surface sized in Example 5 with alkenyl ketene dimer and with SMA copolymer and with the non-surface sized paper. Results are summarized in Table 2 in the two columns under the heading "Inkjet Quality".

Black ink line growth was measured by visual evaluation of line growth by feathering or wicking, i.e., spreading of ink beyond the printed line borders, as described in Example 3. Results are summarized qualitatively in Table 2 above, under the column heading "Black Ink Line Growth".

The results shown in Table 2 indicate no significant differences in black ink line growth among all of the surface-sized papers evaluated. Consequently, the two ketene multimers of the present invention provide print quality, as measured by black ink line growth, that is equivalent to conventional surface sizes, at the addition levels studied, but that significantly less of the 2-oxetanone multimer sizing agent was required compared to the SMA copolymer sizing agent.

Black ink front optical density values were obtained as described in Example 3; high optical density values are desirable since they indicate good quality, dense black ink printing. The results, shown in the penultimate column of Table 2, show that the ketene multimer surface sizes generally provided black ink optical density values at least comparable to the SMA copolymer surface sizing agent, at all levels tested. Paper surface sized with the alkenyl

ketene multimer made using azelaic acid as the dicarboxylic acid provided black ink optical density values comparable to those for the SMA copolymer surface sized paper and comparable to those for the alkenyl ketene dimer surface sized paper, over the range of addition amounts calculated. As before, more of the SMA copolymer sizing agent was needed for the same level of optical density achieved by the sizing agent of this invention.

The results shown in Table 2 indicate that the ketene multimer surface sizing agents evaluated are cost effective replacements for a conventional polymeric surface sizing agent like styrene/maleic anhydride copolymer, for paper grades requiring good inkjet printing quality.

Example 7

The surface sized paper produced with the two ketene multimers in Example 5 was evaluated for photocopier toner adhesion in this Example. The same evaluation was carried out with the paper surface sized in Example 5 with alkenyl ketene dimer and with SMA copolymer and with the non-surface sized paper. The procedures used to evaluate toner adhesion on the paper was identical to that described earlier for Example 4. Results are summarized in Table 2 above, where photocopier toner adhesion values are reported in the last column. As explained in Example 4, low values indicate good toner adhesion.

Paper surface sized with the alkenyl ketene dimer exhibited toner adhesion values that were significantly worse, over the entire addition range studied, than those obtained with SMA copolymer surface sized paper or with the two alkenyl ketene multimer surface sized papers of the present invention. Papers surface sized with SMA copolymer or with the two alkenyl ketene multimer surface sizes had toner adhesion generally comparable to that obtained for the

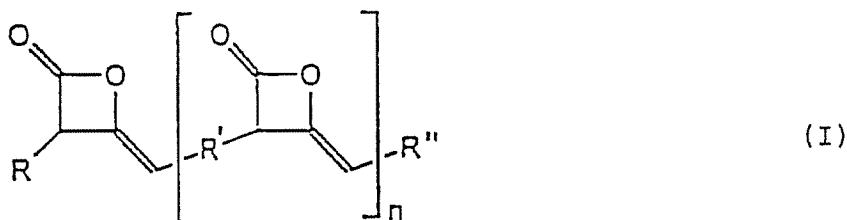
paper containing no surface size (but including an internal size, as did all of the surface sized papers).

5 Use of the two alkenyl ketene multimers as surface sizing agents resulted in generally satisfactory toner adhesion, essentially similar to that provided by the SMA copolymer surface sized paper or the untreated controls. Based on these results, the alkenyl ketene multimers of the present invention are expected to be more efficient sizing agents than traditional polymeric surface sizing agents, 10 without the toner adhesion problems associated with ketene dimer sizing agents.

15 It is not intended that the Examples given here should be construed to limit the invention, but rather they are submitted to illustrate some of the specific embodiments of the invention. Various modifications and variations of the present invention can be made without departing from the scope of the appended claims.

What is claimed is:

1. A method of sizing paper which comprises surface sizing paper with a sizing agent that is a 2-oxetanone multimer that is not solid at a temperature of 35°C.
2. The method of claim 1 wherein the sizing agent is a liquid at 35°C.
3. The method of claim 1 where the sizing agent comprises a mixture of 2-oxetanone multimers that is not solid at a temperature of 35°C.
4. The method of claim 3 wherein at least 25 weight percent of the mixture comprises the 2-oxetanone multimers containing hydrocarbon substituents with irregularities, the hydrocarbon substituents with irregularities being selected from the group consisting of branched alkyl, linear alkenyl and branched alkenyl groups.
5. The method of claim 1 wherein the 2-oxetanone multimer has the formula (I)



in which n is an integer of at least 1;

R and R'' are independently acyclic hydrocarbons of at least about 4 carbon atoms; and

R' is a branched, linear or alicyclic hydrocarbon of about 1 to about 40 carbon atoms.

6. The method of claim 5 wherein, in the formula (I), n is an integer of 1 to about 20.

7. The method of claim 5 wherein, in the formula (I), n is an integer of 1 to about 8.

8. The method of claim 5 wherein the sizing agent comprises a mixture of 2-oxetanone multimers having the formula (I).

9. The method of claim 8 wherein, in the mixture of 2-oxetanone multimers, the average n , in the formula (I), for the mixture of multimers is about 1 to about 8.

10. The method of claim 8 wherein the sizing agent mixture contains about at least 25 weight percent of 2-oxetanone multimers in which irregularities are present in R or R'' or both, where the irregularities are selected from the group consisting of branched alkyl, linear alkenyl and branched alkenyl groups.

11. The method of claim 5 wherein, in the formula (I), R and R'' are independently branched alkyl or linear alkyl or branched alkenyl or linear alkenyl.

12. The method of claim 11 wherein, in the formula (I), R and R'' have about 10 to about 20 carbon atoms.

13. The method of claim 5 wherein, in the formula (I), R' is selected from the group consisting of C_2 - C_{12} hydrocarbon and C_{20} - C_{40} hydrocarbon.

14. The method of claim 13 wherein, in the formula (I), R' is a branched or alicyclic hydrocarbon having about 28 to about 32 carbon atoms.

15. The method of claim 13 wherein, in the formula (I), R' is a linear alkyl having about 4 to about 8 carbon atoms.

16. The method of claim 8 which further comprises preparing the mixture of 2-oxetanone multimers from a mixture of an unsaturated fatty acid mixture and a dicarboxylic acid.

17. The method of claim 16 wherein the fatty acid is selected from the group consisting of oleic, linoleic, linolenic, palmitoleic, and mixtures thereof.

18. The method of claim 16 wherein the dicarboxylic acid is selected from the group consisting of azelaic acid, sebacic acid, dodecanedioic acid, a fatty acid dimer acid and mixtures thereof.

19. The method of claim 17 wherein the dicarboxylic acid is selected from the group consisting of azelaic acid, sebacic acid, dodecanedioic acid, a fatty acid dimer acid and mixtures thereof.

20. The method of claim 1 which further comprises adding the surface sizing agent to a size press in a papermaking process.

21. The method of claim 20 which further comprises adding the surface sizing agent to the size press in an amount sufficient to provide at least about 0.0025 wt%

sizing agent, based on the weight of dry sized paper produced.

22. The method of claim 1 which further comprises adding an internal sizing agent to paper furnish from which the paper is made.

23. The method of claim 22 wherein the internal sizing agent is selected from the group consisting of alkyl ketene dimer, alkyl ketene multimer, alkenyl ketene dimer, alkenyl ketene multimer, alkyl succinic anhydride, alkenyl succinic anhydride, rosin and mixtures thereof.

24. The method of any of claims 1 to 23 which further comprises preparing the 2-oxetanone multimer or mixture of 2-oxetanone multimers from a reaction mixture of fatty acid and dicarboxylic acid in a mole ratio of from about 1:1 to about 1:5 fatty acid to dicarboxylic acid.

25. The method of claim 24 wherein the mole ratio is from about 1:1.5 to about 1:4.

26. The method of claim 24 wherein the reaction mixture contains a molar excess of dicarboxylic acid up to a mole ratio of about 1:5 fatty acid to dicarboxylic acid.

27. The method of claim 24 wherein the mole ratio is about 1:2.

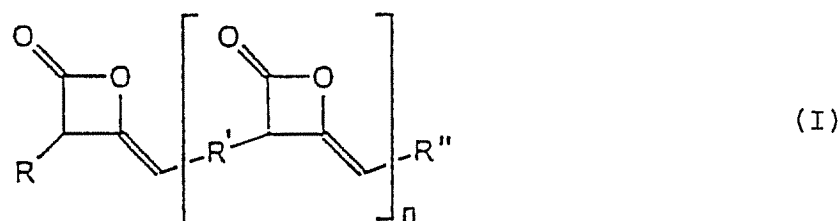
28. Paper surface sized with a sizing agent that is a 2-oxetanone multimer that is not solid at a temperature of 35°C.

29. The surface sized paper of claim 28 wherein the sizing agent is a liquid at 35°C.

30. The surface sized paper of claim 28 wherein the sizing agent comprises a mixture of 2-oxetanone multimers that is not solid at a temperature of 35°C.

31. The surface sized paper of claim 30 wherein at least 25 weight percent of the mixture comprises the 2-oxetanone multimers containing hydrocarbon substituents with irregularities, the hydrocarbon substituents with irregularities being selected from the group consisting of branched alkyl, linear alkenyl and branched alkenyl groups.

32. The surface sized paper of claim 28 wherein the 2-oxetanone multimer has the formula (I)



in which n is an integer of at least 1;

R and R'' are independently acyclic hydrocarbons of at least about 4 carbon atoms; and

R' is a branched, linear or alicyclic hydrocarbon of about 1 to about 40 carbon atoms.

33. The surface sized paper of claim 32 wherein, in the formula (I), n is an integer of 1 to about 20.

34. The surface sized paper of claim 32 wherein, in the formula (I), n is an integer of 1 to about 8.

35. The surface sized paper of claim 32 wherein the sizing agent comprises a mixture of 2-oxetanone multimers having the formula (I).

36. The surface sized paper of claim 35 wherein, in the mixture of 2-oxetanone multimers, the average n , in the formula (I), for the mixture of multimers is about 1 to about 8.

37. The surface sized paper of claim 35 wherein the sizing agent mixture contains about at least 25 weight percent of 2-oxetanone multimers in which irregularities are present in R or R'' or both, where the irregularities are selected from the group consisting of branched alkyl, linear alkenyl and branched alkenyl groups.

38. The surface sized paper of claim 32 wherein, in the formula (I), R and R'' are independently branched alkyl or linear alkyl or branched alkenyl or linear alkenyl.

39. The surface sized paper of claim 38 wherein, in the formula (I), R and R'' have about 10 to about 20 carbon atoms.

40. The surface sized paper of claim 32 wherein, in the formula (I), R' is selected from the group consisting of C_2 - C_{12} hydrocarbon and C_{20} - C_{40} hydrocarbon.

41. The surface sized paper of claim 40 wherein, in the formula (I), R' is a branched or alicyclic hydrocarbon having about 28 to about 32 carbon atoms.

42. The surface sized paper of claim 40 wherein, in the formula (I), R' is a linear alkyl having about 4 to about 8 carbon atoms.

43. The surface sized paper of claim 35 which further comprises preparing the mixture of 2-oxetanone

multimers from a mixture of an unsaturated fatty acid mixture and a dicarboxylic acid.

44. The surface sized paper of claim 43 wherein the fatty acid is selected from the group consisting of oleic, linoleic, linolenic, palmitoleic, and mixtures thereof.

45. The surface sized paper of claim 43 wherein the dicarboxylic acid is selected from the group consisting of azelaic acid, sebacic acid, dodecanedioic acid, a fatty acid dimer acid and mixtures thereof.

46. The surface sized paper of claim 44 wherein the dicarboxylic acid is selected from the group consisting of azelaic acid, sebacic acid, dodecanedioic acid, a fatty acid dimer acid and mixtures thereof.

47. The surface sized paper of claim 28 which further comprises an internal sizing agent.

48. The surface sized paper of claim 47 wherein the internal sizing agent is selected from the group consisting of alkyl ketene dimer, alkyl ketene multimer, alkenyl ketene dimer, alkenyl ketene multimer, alkyl succinic anhydride, alkenyl succinic anhydride, rosin and mixtures thereof.

49. The surface sized paper of claim 28 wherein the sizing agent is present on the sized paper in an amount of from about 0.0025 wt% to about 0.5 wt%, based on the weight of the dry sized paper.

50. The surface sized paper of claim 28 wherein the paper is selected from the group consisting of paper, newsprint, paperboard and molded paper.

51. The surface sized paper of claim 28 wherein the paper is selected from the group consisting of continuous forms bond paper, cut copy paper, envelope-making paper, offset printing paper, inkjet printing paper and adding machine paper.

52. The surface sized paper of any of claims 28 to 51 which further comprises preparing the 2-oxetanone multimer or mixture of 2-oxetanone multimers from a reaction mixture of fatty acid and dicarboxylic acid in a mole ratio of from about 1:1 to about 1:5 fatty acid to dicarboxylic acid.

53. The surface sized paper of claim 52 wherein the mole ratio is from about 1:1.5 to about 1:4.

54. The surface sized paper of claim 52 wherein the reaction mixture contains a molar excess of dicarboxylic acid up to a mole ratio of about 1:5 fatty acid to dicarboxylic acid.

55. The surface sized paper of claim 52 wherein the mole ratio is about 1:2.

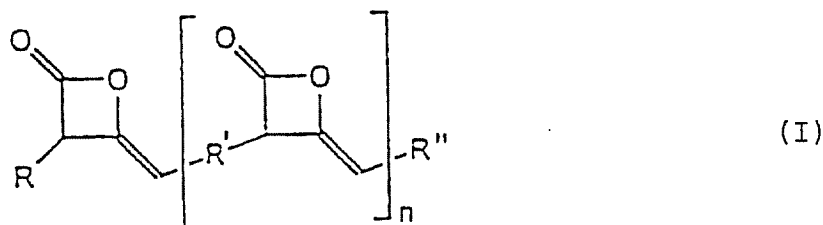
56. A sizing agent which comprises a 2-oxetanone multimer that is not solid at a temperature of 35°C and that is prepared from a reaction mixture of fatty acid and dicarboxylic acid having a molar excess of dicarboxylic acid.

57. The sizing agent of claim 56 which is a liquid at 35°C.

58. The sizing agent of claim 56 where the sizing agent comprises a mixture of 2-oxetanone multimers that is not solid at a temperature of 35°C.

59. The sizing agent of claim 58 wherein at least 25 weight percent of the mixture comprises multimers containing hydrocarbon substituents with irregularities, the hydrocarbon substituents with irregularities being selected from the group consisting of branched alkyl, linear alkenyl and branched alkenyl groups.

60. The sizing agent of claim 56 wherein the 2-oxetanone multimer has the formula (I)



in which n is an integer of at least 1;

R and R'' are independently acyclic hydrocarbons of at least about 4 carbon atoms; and

R' is a branched, linear or alicyclic hydrocarbon of about 1 to about 40 carbon atoms.

61. The sizing agent of claim 60 wherein, in the formula (I), n is an integer of from 1 to about 20.

62. The sizing agent of claim 60 wherein, in the formula (I), n is an integer of 1 to about 8.

63. The sizing agent of claim 60 wherein the sizing agent comprises a mixture of 2-oxetanone multimers having the formula (I).

64. The sizing agent of claim 63 wherein, in the mixture of 2-oxetanone multimers, the average n , in the formula (I), for the mixture of multimers is about 1 to about 8.

65. The sizing agent of claim 63 wherein the sizing agent mixture contains about at least 25 weight percent of 2-oxetanone multimers in which irregularities are present in R or R" or both, where the irregularities are selected from the group consisting of branched alkyl, linear alkenyl and branched alkenyl groups.

66. The sizing agent of claim 60 wherein, in the formula (I), R and R" are independently branched alkyl or linear alkyl or branched alkenyl or linear alkenyl.

67. The sizing agent of claim 66 wherein, in the formula (I), R and R" have about 10 to about 20 carbon atoms.

68. The sizing agent of claim 60 wherein, in the formula (I), R' is selected from the group consisting of C₂-C₁₂ hydrocarbon and C₂₀-C₄₀ hydrocarbon.

69. The sizing agent of claim 68 wherein, in the formula (I), R' is a branched or alicyclic hydrocarbon having about 28 to about 32 carbon atoms.

70. The sizing agent of claim 68 wherein, in the formula (I), R' is a linear alkyl having about 4 to about 8 carbon atoms.

71. The sizing agent of claim 63 wherein the mixture of 2-oxetanone multimers is prepared from a mixture of an unsaturated fatty acid mixture and a dicarboxylic acid.

72. The sizing agent of claim 71 wherein the fatty acid is selected from the group consisting of oleic, linoleic, linolenic, palmitoleic, and mixtures thereof.

73. The sizing agent of claim 71 wherein the dicarboxylic acid is selected from the group consisting of azelaic acid, sebacic acid, dodecanedioic acid, a fatty acid dimer acid and mixtures thereof.

74. The sizing agent of claim 72 wherein the dicarboxylic acid is selected from the group consisting of azelaic acid, sebacic acid, dodecanedioic acid, a fatty acid dimer acid and mixtures thereof.

75. The sizing agent of claim 56 wherein the 2-oxetanone multimer is a surface size.

76. The sizing agent of any of claims 56 to 75 wherein the reaction mixture of fatty acid and dicarboxylic acid has a mole ratio of from about 1:1.5 to about 1:5 fatty acid to dicarboxylic acid.

77. The sizing agent of claim 76 wherein the mole ratio is about 1:2.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 96/12172

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H17/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 0 666 368 A (HERCULES INC) 9 August 1995 cited in the application see the whole document ---	1-77
E	EP 0 742 315 A (HERCULES INC) 13 November 1996 see the whole document ---	56-77
A	EP 0 624 579 A (HERCULES INC) 17 November 1994 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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24 January 1997

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/12172

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